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XXXI. *On the Properties of Electro-deposited Antimony* (continued). By G. GORE, Esq.  
*Communicated by Professor TYNDALL, F.R.S.*

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a. *Heat of discharge not due to cohesive action.*

59. I HAVE already shown to some extent that the change observed in electro-deposited antimony is not an instance of cohesive force exercised between the particles of the metal, because extensive fractures may occur in the mass (16. 17.) without producing or materially influencing the change; and the cohesion of the particles may be indefinitely reduced by triturating the metal to a very fine powder (30. 31. 32.) without a corresponding reduction taking place in the amount of heat evolved. Heat also, which decreases the cohesive force, increases the molecular energy (28.).

60. To test the question further, I took a quantity of small pieces of unchanged antimony, averaging about  $\frac{1}{4}$ th of an inch square and  $\frac{1}{16}$ th of an inch thick, divided it into two portions, reduced one portion to a very fine powder in water at 45° FAHR., dried it in the open air, and finally with a gentle heat. I then placed 300 grains of the powder in a short test-tube closed by a cork, and surrounded by 400 grains of distilled water contained in a small glass beaker covered with cotton-wool; and when the whole had acquired a temperature of 53°·2 FAHR., I induced the change by means of a heated wire, and agitated the water until a thermometer in it indicated a maximum temperature of 72°·5 FAHR. = a rise of 19·3 degrees. The powder was then removed, and a perfectly similar experiment made with 300 grains of the unpulverized fragments, in which case the temperature of 400 grains of water rose from 52°·8 FAHR. to 72°·2 FAHR. = a rise of 19·4 degrees.

61. I also took a freshly formed bar† of the unchanged substance, perfectly free from grey antimony,  $\frac{1}{4}$ th of an inch thick and  $1\frac{1}{4}$  inch long, weighing 278·92 grains; and the same weight of a mixture of small fragments and particles of similar metal, and made two similar experiments to those described; the weight of water in each experiment being 403·78 grains, and the specific heat-value of the immersed portions of the thermometer and test-tube being = 14·60 grains of water. With the *bar* the temperature of the water, &c. rose 20·05 FAHR. degrees; and with the *fragments* and *particles* it rose 20·00 degrees. The bar lost 9·80 grains, or 3·51 per cent. of expelled vapour, 9·72 grains of which was found condensed in the tube in the form of a thick buttery substance, evidently terchloride of antimony.

\* Subsequently revised and condensed by the author.

† *Bars* are formed by depositing the substance upon narrow strips of sheet silver, the edges of which are enclosed by vertical borders of white wax (see 90.).

62. And as a final settlement of this question, I took a bar weighing 277.16 grains, and the same weight of very finely powdered active antimony formed at the same period, and made two more experiments, the weight of water in each instance being 401.14 grains, and the specific heat-value of the thermometer and tube being =14.6 grains of water. With the *bar*, the water rose in temperature from 59°3 to 78°4 FAHR., and with the *powder* it rose from 58°9 to 78°0 FAHR., equal in each case to a rise of 19.1 FAHR. degrees. The loss of weight in the bar was 9.42 grains, or 3.39 per cent., and the amount of condensed vapour found in the tube was 9.26 grains.

63. After making a small deduction for loss of heat by particles which may have undergone the change during the process of grinding, it is evident that the amount of heat set free by the powdered substance is not sensibly different from that evolved by the substance in the coherent massive state, and therefore the force exercised in the peculiar change of antimony is not that of cohesion.

64. The only method by which I have yet been able approximately to determine the amount of changed antimony contained in the powder, or the extent to which the powder has lost its peculiar thermic power, has been to measure the amount of heat evolved by the discharge of a given weight of it in a calorimeter.

*b. Heat of discharge not due to alteration of specific heat.*

65. It may readily be supposed that a portion of the evolved heat may be due to diminution of specific heat attendant upon the increase of specific gravity which occurs during the sudden change (46.); I therefore made several determinations of the specific heat of unchanged and changed specimens in an apparatus similar to that used by REGNAULT for specific heats. The specimen to be examined was placed in a small copper wire basket, suspended by a horsehair, and raised by means of small pulleys into a vertical cylindrical air-chamber, surrounded by a vessel of hot water, and retained there in contact with the bulb of a thermometer until it had acquired a perfectly uniform and stationary temperature (generally about 160° or 180° FAHR.) by careful regulation of the heat. Meanwhile a known quantity of distilled water (usually an equal weight to the antimony) in a thin glass vessel covered externally with cotton-wool, and containing a thermometer, was brought to a uniform and stationary temperature (generally about 60° FAHR.) by surrounding it by non-conducting screens. At that moment the vessel of water was placed close beneath the air-chamber, and the basket lowered in an instant into the water by means of the horsehair and pulleys. The vessel of water was immediately removed and closed, and the basket agitated continually by means of a hooked glass rod passing through a hole in the cover until the thermometer indicated a maximum temperature, which occurred in about two minutes. Corrections in the calculation were made in each instance for the amount of heat evolved by the basket, and for that absorbed by the immersed portion of the thermometer.

66. Seven determinations were made of the specific heat of two unchanged bars, each weighing upwards of 250 grains, and the following numbers were obtained, in the

order given,—0·06405, 0·06261, 0·06204, 0·06372, 0·06329, 0·06240, and 0·06377; mean 0·06312. The discharging point of perfectly similar bars was  $205^{\circ}\cdot5$  FAHR., and the highest temperature to which these were raised was  $185^{\circ}\cdot3$  FAHR.; nevertheless on several occasions during their presence in the air-bath at the higher temperatures I observed that they evolved heat; and after the experiments, I found that they had entirely lost their heating property: their weights and specific gravities were, however, but very slightly different from those found before the specific heat determinations, but their fractured surfaces were much less bright and of a lighter colour than those of unchanged antimony. From these experiments it appears that the discharge of heat by electro-deposited antimony is not necessarily attended by alteration of the specific heat of the substance; because whilst the substance was *gradually* discharging the whole of its peculiar heat, its specific heat did not sensibly diminish, as may be observed by examining the numbers obtained.

67. An extra determination was made with two similar bars, weighing together upwards of 480 grains; raising their temperature only to  $118^{\circ}\cdot0$  FAHR., the number obtained was 0·0637; they still possessed the heating property, evidently because they had not been subjected to a sufficiently high temperature to produce even a gradual discharge. The specific heat of the solution in which the bars were formed was found by the method of cooling to be  $=0\cdot6550$ .

68. Some determinations of the specific heat of antimony which had been *suddenly* discharged were also made. With two bars which had been changed in air at  $60^{\circ}$  FAHR., and weighing together about 730 grains, the following successive numbers were obtained,—0·0533, 0·0545, 0·0549, 0·0547; mean  $=0\cdot0543$ . And with thin pieces discharged in the hot-air bath, and weighing nearly 740 grains, the numbers 0·0522 and 0·0533 were obtained. The results were checked by separate determinations of the specific heat of purified antimony in the ordinary state of aggregation. The manifest reason why the specific heat of the *suddenly* changed bars was less than that of the *gradually* changed ones, was because they had by the *sudden* discharge been subjected to a very much higher temperature, and had therefore lost a larger proportion of their enclosed liquid, which is a substance of greater specific heat than metallic antimony. A similar reason explains why the thin pieces suddenly discharged in a heated atmosphere had less specific heat than the bars suddenly discharged in cool air. In all cases, the higher the temperature the substance had been subjected to in the process of discharge,—either by being suddenly instead of gradually discharged, or by being suddenly discharged in a non-conducting heated medium instead of in cool air (or in cold water or mercury, for example), or by discharging a large bulk instead of a small quantity,—the greater was the loss of enclosed liquid, increase of specific gravity, and decrease of specific heat.

*c. Temperature at which the sudden discharge occurs.*

69. A number of experiments were made to ascertain the temperature at which the substance discharges its heat, in the following manner:—two perfectly similar specimens

were taken; one was suspended in the air-bath of the calorimeter and heated with moderate speed until the discharge occurred, to determine *approximately* its discharging point; the second was then tried, raising the temperature of the bath with increasing slowness until within ten to four degrees of the discharging point; the bath being then kept stationary at that temperature, the metal began to evolve its heat, raising its own temperature above that of the bath, slowly at first, and then more quickly, until the sudden discharge took place. In some cases, where the quantity of metal operated upon was small, and especially if the temperature of the surrounding bath was a few degrees too low, the heat was evolved *gradually* without any sudden discharge.

	grains.		° FAHR.	
1. Coarse granules (freshly formed)	350.00	in a fine brass gauze basket.	Discharged suddenly at 206.3	{ and lost 4.07 per cent. in vapour.
2. Bars and thin pieces (stale) .....	600.00	in a thin copper bucket.....	Discharged suddenly at 205.5	
3. Thin pieces (stale) .....	572.27	in a thin copper bucket.....	Discharged suddenly at 198.0	
4. Thin pieces (freshly formed).....	96.16	in a thin copper bucket.....	Discharged suddenly at 196.5	
5. Bars (formed one day) .....	249.78	in a fine brass gauze basket	Discharged suddenly at 196.0	{ and lost 4.70 per cent. in vapour.
6. Bars (recently deposited) .....	605.09	in a thin copper bucket.....	Discharged suddenly at 184.0	
7. Lumps (recently deposited) .....	445.24	in a thin copper bucket.....	Discharged suddenly at 183.1	
8. Powder (stale) .....	307.77	in a closed brass vessel .....	Discharged suddenly at 178.0	
9. Powder, but had been kept in a warm place .....	195.70	in a closed brass vessel .....	{ Discharged gradually during two minutes at } 172.0	
10. Powder, but had been kept in a warm place .....	300.00	in a closed brass vessel .....	{ Discharged suddenly but feebly at ..... } 171.0	
11. Fine powder .....	300.00	in a thin copper bucket.....	Discharged suddenly at 166.0	

In a former experiment (35.), with less perfectly amorphous metal, a much higher temperature of discharge was observed, partly because a bath of mercury was employed which conveyed the evolved heat more rapidly away.

70. It is probable that the real temperature of sudden discharge is above  $212^{\circ}0$  FAHR., because the temperature observed in each of the above experiments was only that of the *external surface* of the basket; the *centre* of the mass or heap of antimony was probably at a much higher temperature. It also appears that the discharge is not limited to a particular temperature, but commences between  $170^{\circ}$  and  $190^{\circ}$  FAHR., and gradually increases in rapidity to some point above  $212^{\circ}$  FAHR., when it attains its maximum, and becomes sudden.

71. Small thin pieces of the substance formed at the same period, and in the same liquid as those of Nos. 4 and 6, were heated a few minutes in water at  $209^{\circ}$  FAHR., and in air at  $203^{\circ}$  FAHR. without losing their heating power; but by immersing them in boiling water during twenty minutes, nearly the whole of the heating power was removed without loss of weight in the pieces. Two portions of 20 grains each were also placed, one in a fine brass wire-gauze vessel, and the other in a water-tight copper bucket, and both immersed in boiling water during thirty minutes: at the end of that time the heating power of each had disappeared; the former had gained 0.11 grain in weight (probably by absorption of water), and the weight of the latter had remained unaltered.

72. The thermic power may be exhausted either gradually or suddenly, and the conditions of gradual or sudden discharge appear to be these:—if the amount of cooling

influences is great in relation to the amount of heat to be discharged the action is gradual, but if it is small the action is sudden.

d. *Total amount of heat evolved by the change.*

73. The following determinations were made of the total amount of heat evolved during the change. In each instance the metal was contained in a fine brass gauze basket with a lid, placed in a glass tube immersed in the water of a small calorimeter, and its heat was discharged by contact of a small heated wire momentarily introduced through a hole in the cork of the tube and in the lid. The water was constantly stirred, and it occupied about nine minutes in attaining its maximum temperature. The calculations include the heat absorbed by the basket, the immersed portions of the tube and thermometer, the water, and the metallic mass; reckoning the terchloride of antimony and actual metal *together*, i. e. as one mass, possessing a mean specific heat of 0.06312 (see 66.).

grains.		Evolved sufficient heat to raise its own weight of antimony, of specific heat 0.0508.	grains.
1. 300.0	of coarse granules, deposited 1 day	666.27 FAHR. degrees; and lost 10.81 of expelled vapour = 3.6	per cent.
2. 350.0	of coarse granules, deposited 2 days	662.38 FAHR. degrees; and lost 12.74 of expelled vapour = 3.64	per cent.
3. 350.0	of coarse granules, deposited 2 days	664.64 FAHR. degrees; and lost 12.52 of expelled vapour = 3.57	per cent.
4. 350.0	of coarse granules, deposited 2 days	657.95 FAHR. degrees; and lost 12.00 of expelled vapour = 3.42	per cent.
5. 350.0	of coarse granules, deposited 3 days	620.29 FAHR. degrees; and lost 12.49 of expelled vapour = 3.56	per cent.
6. 300.0	of thin pieces, deposited 1 day	705.89 FAHR. degrees; and lost 11.13 of expelled vapour = 3.71	per cent.
7. 300.0	of fine powder, deposited 6 weeks	602.84 FAHR. degrees; and lost 2.33 of expelled vapour = 0.776	per cent.
8. 300.0	of thin pieces, deposited 6 hours	651.78 FAHR. degrees; and lost 11.26 of expelled vapour = 3.75	per cent.
9. 272.42	a bar, deposited 1 day	628.70 FAHR. degrees; and lost 7.55 of expelled vapour = 2.43	per cent.
10. 400.0	of thin pieces, deposited 3 hours	655.35 FAHR. degrees; and lost 15.49 of expelled vapour = 3.87	per cent.
11. 251.92	a bar	633.06 FAHR. degrees; and lost 10.8 of expelled vapour = 4.28	per cent.

The coarse granules used in experiments 1 to 5 were formed by depositing the substance upon coarse copper wire-gauze, and bending the coated gauze backwards and forwards in cold water, then sifting and drying the product. The metal of No. 7 had been previously exposed for two hours in the air-bath to a uniform temperature of 152° FAHR., and during that time had lost 0.05 grain in weight.

74. A bar of active antimony rapidly deposited in a nearly pure solution of acid hydrochlorate of terchloride of antimony, taken from the liquid, and discharged the same day in the calorimeter at 65°·5 FAHR., evolved sufficient heat to raise the temperature of its own weight of ordinary antimony (specific heat = 0.0508) 624.65 FAHR. degrees. The following are the specific heat-values in water of the materials and apparatus:—

Antimony	..... 356.27 grs. (sp. heat = 0.06312) =	22.4877 grs. of water	} Raised from 65°·5 FAHR. to 79°·0 FAHR. = 13.5 degrees.
Brass basket	..... (sp. heat = 0.0939) =	5.0696 grs. of water	
Immersed part of glass tube	(sp. heat = 0.1770) =	28.718 grs. of water	
Mercury of thermometer	... (sp. heat = 0.0330) =	6.832 grs. of water	
Water	.....	774.320 grs.	
837.4273 grs. of water			

The discharge in this instance was quite instantaneous, and shattered the bar into

minute fragments. The loss of weight by evolved vapour was 5.99 grains = 1.68 per cent. In several cases, when the substance has been rapidly deposited and discharged within a short period, the action has been instantaneous, and the metal has been shattered into minute particles (see 25.).

*e. The evolution of vapour not a cause but an effect of the heat.*

75. The evolution of vapour and consequent loss of weight by the discharge appears to be entirely dependent upon the temperature which the substance acquires during the discharge. 1st. If the substance acquires a very high temperature, such as when it is discharged in a hot-air bath, its loss of weight is considerable; but if it does not acquire a very high temperature, as when it is gradually discharged by suspending it in a hot-air bath at about 150° or 170° FAHR., or in a hot-water bath at 212° FAHR., its loss of weight is very small. The following experiments will illustrate this statement:—

Three perfectly similar bars, taken the previous day from the depositing liquid, were separately discharged in the hot-air bath: the first was gradually raised in temperature during one hour and forty minutes from 60° to 196° FAHR., it then suddenly discharged with considerable force; the second was maintained at a temperature varying from 170° to 178° FAHR. during two hours and eleven minutes, it then suddenly discharged its heat with less force; and the third was kept at a temperature varying from 170° to 177° FAHR. during nine hours and twelve minutes, and (after the heat appeared to be all discharged) during the last two hours at 180° FAHR., and finally at 186° FAHR.; it evolved its heat gradually without any sudden discharge, and was found to have entirely lost its thermic power. The following are the weights of the bars, their specific gravities, their losses of vapour, &c.:—

Before the experiment.

No. 1.	grains. 249.78.	
No. 2.	254.65.	Specific gravity 5.811 at 66° FAHR.
No. 3.	299.65.	Specific gravity 5.825 at 63° 3 FAHR.

After the experiment.

	grains.	grains.	
No. 1.	238.02	lost 11.76	= 4.7 per cent.
No. 2.	248.68	lost 5.95	= 2.34 per cent.
No. 3.	297.41	lost 2.24	= 0.747 per cent. Specific gravity 5.853 at 62° 6 FAHR.

Also two perfectly similar bars, the first weighing 251.92 grains, and the second weighing 256.18 grains, were deprived of their energy; the first *suddenly* in the air-bath of the calorimeter at 60° FAHR., and the second *gradually* by suspending it in boiling water during six hours. The first one lost 10.8 grains = 4.28 per cent., and the second lost 0.73 grain = 0.28 per cent.; and another bar, weighing 256.18 grains, was immersed in cold water, the water heated to boiling in thirty minutes, and kept boiling during six

hours: the bar was then taken out; it had lost the whole of its heating power, and weighed 275·6 grains = a loss of 0·26 per cent. in weight.

And 2nd. If two pieces of active antimony are suddenly discharged, and from any cause the temperatures they acquire are different, the amounts of vapour they evolve are also different; thus a quantity of thin fragments was divided into equal parts of 180 grains each; the first was placed in a fine brass wire-gauze basket with a wire-gauze lid, and raised quickly to a temperature of 163°·0 FAHR. in the air-bath, and then at once discharged in the open air at 60° FAHR., by momentary contact of a heated wire; and the second portion, placed in the same basket, was surrounded by ice and cooled to 34° FAHR., and similarly discharged in the air at 60° FAHR.; the former evolved its heat instantaneously, and lost 8·85 grains, or 4·916 per cent. in weight; and the latter discharged feebly and much less rapidly, and lost 5·40 grains, or 3·00 per cent. It appears from these various experiments that the evolution of vapour is not a cause nor even a necessary consequence of the change, but only occurs when the temperature of the substance during the discharge is considerably raised; and it makes no difference whether the requisite temperature is acquired by means of internal heat or by heat from external sources.

76. In all instances, and these were very numerous, the heat from the discharge alone was insufficient to expel more than three-fourths of the contained liquid, and in those instances, whether of sudden or gradual discharge, the remainder, making a total in each case of upwards of *six* per cent., was always readily expelled by fusing the metal in a test-tube.

*f. Influence of temperature upon the amount of heat evolved.*

77. Two similar bars were taken, No. 1 weighing 257·21 grains, and No. 2 weighing 245·90 grains: the first was placed in the wire-gauze basket and cooled to 34°·0 FAHR., then at once transferred to the calorimeter (which was at 57°·6 FAHR.), and instantly discharged; the second was also placed in a similar basket and heated to 157°·15 FAHR. in the air-bath; the basket and bar were then instantly lowered into the calorimeter (which was at 57°·75 FAHR.), and at once discharged; the calorimeter of the former attained a maximum temperature of 67°·35 FAHR. in nine minutes, and of the latter a maximum of 69°·4 FAHR. in the same period. The following are the various specific heat-values in water of the substances, &c.:—

No. 1.

Antimony.....	257·21 grains (sp. heat = 0·06312) =	16·235 grains of water	} Raised from 34°·0 to 67°·35 FAHR. = 33·35 degrees.
Brass basket .....	(sp. heat = 0·0939 ) =	6·242 grains of water	
		22·477 grains of water	

Immersed part of glass tube of calorimeter (sp. heat = 0·1770) =	28·718 grs. of water	} Raised from 57°·6 to 67°·35 FAHR. = 9·75 degrees.
Mercury of thermometer.....(sp. heat = 0·033 ) =	2·070 grs. of water	
Portion of stem of thermometer.....(sp. heat = 0·1770) =	3·600 grs. of water	
Water of calorimeter .....	743·764 grs.	
	778·152 grs. of water	



The thermic discharge in this case was rather feeble and slow, and the loss of vapour was 7.79 grains = 3.02 per cent. The amount of heat evolved by the bar was sufficient to raise the temperature of its own weight of ordinary antimony (of specific heat 0.0508) 638.022 FAHR. degrees.

## No. 2.

Antimony.....	245.90 grains (sp. heat=0.06312)=15.521 grains of water	} Fell from 157°15 to 69°4 FAHR.=87.75 degrees.
Brass basket.....	(sp. heat=0.0939 )= 6.346 grains of water	
	<u>21.867</u> grains of water	

Immersed part of glass tube of calorimeter (sp. heat=0.1770)=	28.718 grs. of water	} Rose from 57°75 to 69°4 FAHR. =11.65 degrees.
Mercury of thermometer.....(sp. heat=0.033 )=	2.070 grs. of water	
Portion of stem of thermometer .....	(sp. heat=0.1770)= 3.600 grs. of water	
Water of calorimeter .....	<u>773.272</u> grs.	
	804.660 grs. of water	

The discharge in this instance was instantaneous and powerful, and the loss of vapour was 13.06 grains=5.311 per cent. The amount of heat evolved by the bar was sufficient to raise the temperature of its own weight of ordinary antimony 732.829 FAHR. degrees. It appears from these experiments that the amount of heat evolved by the peculiar change of antimony varies with the temperature at which the discharge occurs, and is greater at high temperatures than at low ones, similar to the specific heat of substances. These experiments also confirm the previous ones (75.) with regard to the absence of relation of the amount of evolved heat to that of evolved vapour; if the amount of heat varied with the amount of vapour, it would, in the second of these experiments, have been sufficient to have raised the temperature of the given weight of ordinary antimony 1069.64 FAHR. degrees, instead of 732.829 degrees.

*g. Chemical composition of the active substance.*

78. The deposited metal has been repeatedly found by chemical analysis to contain, in addition to terchloride of antimony and hydrochloric acid, small portions of nearly all the impurities which existed in the anode and in the depositing liquid. The small portions of gas and carbon observed in former experiments of fusion (53. 54.), appeared to be due to enclosed traces of tartar-emetic decomposed by the heat.

79. To exclude the possibility of the peculiar property of electro-deposited antimony being dependent upon the presence of impurities, I purified antimony and teroxide of antimony for the anode and solution by several methods. 1st. Some very pure tartar-emetic was projected, in small portions at a time, into a red-hot assay crucible; and the resulting mass of antimonide of potassium removed when cool, triturated with distilled water until all the potash and carbon were removed, and after drying fused with a little cyanide of potassium. 2nd. Some of the best quality of commercial antimony was very finely pulverized and boiled with pure sulphuric acid, the cooled crystalline sulphate washed first with cold and then with hot distilled water until all traces of iron disap-

peared, then heated with a weak solution of ammonia, and finally washed with distilled water until all traces of sulphuric acid were removed, and thoroughly dried at about 300° FAHR. Some of the oxide thus formed was reduced to the metallic state by fusion with cyanide of potassium. 3rd. Best commercial antimony, also electro-deposited grey antimony, was very finely pulverized, the powder boiled nearly to dryness with pure nitric acid, the mass well washed with distilled water, and the process with the acid and water repeated several times to remove iron, copper, and lead; the dried residue was then heated to redness as long as vapours were evolved, and reduced by fusion with twice its weight of cyanide of potassium. And 4th. A hot solution of pure tartar-emetic was precipitated by solution of ammonia, and the resulting teroxide washed with abundance of hot distilled water and dried.

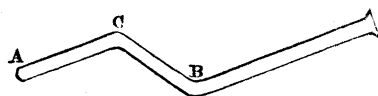
80. Several depositing liquids were prepared by dissolving the purified oxide in pure hydrochloric acid to about two-thirds' or three-fourths' saturation; using the purified metal as anodes, and sheets of platinum as cathodes. The oxide and metal prepared by the second method were used much more extensively than either of the others. With each depositing liquid an abundant deposit of bright black antimony was readily obtained in the usual manner, and the deposited metal possessed the usual structure and peculiar heating power, and evolved the usual vapour during the change.

81. Analyses of two different specimens of the pure unchanged substance deposited from a solution composed of 3 parts of pure hydrochloric acid saturated with pure oxide of antimony and then 1 part more of the acid added, yielded the following results. The first specimen was deposited more rapidly than the second.

No. 1.				No. 2.			
Sb	.	.	93.36	Sb	.	.	93.51
Sb, Cl <sup>3</sup>	.	.	5.98	Sb, Cl <sup>3</sup>	.	.	6.03
H, Cl	.	.	0.46	H, Cl	.	.	0.21
99.80				99.75			

A trace of water contained in them was not estimated.

82. The method of analysis was as follows:—a tube of German glass, nearly half an inch in diameter and 12 inches long, closed at one end, was bent to the annexed figure; the closed end was heated, and 200 grains of unchanged antimony, in small fragments, was introduced, a single fragment at a time, to discharge the heat safely; the metal was then gradually heated to fusion and collected in A, whilst the semisolid distillate collected in B; the two were then separated by fusing the tube at C. The distillate was dissolved in a solution of tartaric acid, and the amount of terchloride of



\* It is worthy of remark, that grey antimony deposited in the crystalline state from the tartaric acid solution (2.), contains only a minute quantity of enclosed liquid, similar to the exclusion of impurities from substances generally by crystallization.

antimony contained in it determined as sulphide by sulphuretted hydrogen, and after separating the excess of sulphuretted hydrogen from the filtrate by adding solution of sulphate of sesquioxide of iron and filtering, the total amount of chlorine was determined as chloride of silver; the amount of chlorine due to the terchloride found was then subtracted, and the remainder estimated as hydrochloric acid.

*h. Is the peculiar change of antimony necessarily attended by a chemical change?*

83. To ascertain whether during the act of *gradual* discharge the acid terchloride of antimony contained in the substance passed from a state of stronger combination with the metal to a state of weaker combination, I took 200 grains of unchanged antimony powder, placed it in equal portions in two small flasks, added to each 500 grains of distilled water; immersed one of the flasks in boiling water during thirty minutes, to discharge the heating power of its metal, and then replaced the evaporated water; added 50 grains of tartaric acid and 106·35 grains of hydrochloric acid to the contents of each flask, and allowed both vessels to remain at 60° FAHR. during two days. The two liquids were then separately filtered, the contents of the filters washed with equal quantities of a solution of tartaric acid, the washed residues dried, the filtrates precipitated by sulphuretted hydrogen, and the precipitates washed and dried. The contents of the heated flask yielded 93·15 grains of metallic residue possessing no heating power, and 4·20 grains of precipitated tersulphide of antimony: the contents of the other flask gave 97·24 grains of residue possessing the heating power, and 1·77 grain of tersulphide. I have also found on other occasions, when the powdered active substance had lost its peculiar property with extreme slowness (see 86.), and its weight and chemical composition had remained unaltered, that the terchloride of antimony contained in it was much more completely and easily extracted by means of solvents than whilst the powder retained its heating power. No appearance of *mechanical mixture* of terchloride of antimony with metallic antimony could be detected in changed powder by means of a powerful microscope.

84. From these observations it appears, that during the act even of gradual discharge, the terchloride of antimony changes from a state of more intimate to a state of less intimate union with the metal; but whether that change consists of diminished *chemical*, or simply diminished *mechanical* union, I have been unable to ascertain.

*i. Can the terchloride of antimony be separated without destroying the heating property?*

85. Several portions of the unchanged powder were digested in strong hydrochloric acid, solution of tartaric acid, and in strongly alkaline liquids for lengthened periods of time, at the atmospheric temperature, with an expectation of extracting at least the greater portion of the terchloride and retaining the whole of the heating power; but it was found that in every instance the heating property gradually diminished, and in about six or seven months entirely disappeared. The loss of heating power was not alone due (if at all, see 86.) to the abstraction of the terchloride by the solvents, because

it occurred in those samples from which only about one-half of the terchloride had been dissolved, as well as in those from which the whole had been extracted (see also 52.).

j. *Does electro-deposited antimony gradually change?*

86. Other portions of each of the samples of powder used in these experiments (85.) were enclosed in well-stoppered bottles, and kept during the same period (seven months) in a cool place not exposed to sunshine; in each instance the heating power entirely disappeared, and the powder became somewhat oxidized and acquired a slightly acid odour from partial separation of the terchloride; several other samples of equal age behaved similarly. Dr. PERCY has also obtained similar results by placing the active powder in a capsule over strong sulphuric acid for several months. Some active powder, exposed to strong daylight during two months, still retained a heating power. Coarse granules of the active substance lost a large portion of their power in seven months: and solid bars, nearly a quarter of an inch thick, which had been formed several months before, and had been more exposed to the atmosphere, were also found to be slightly but distinctly weakened.

87. From these and other observations, it is certain that electro-deposited antimony undergoes a gradual change or decomposition even at 60° FAHR., attended by a diminished union between the terchloride of antimony and metal, and gradual and complete loss of its peculiar heating power, similar to its change in heated air at 160° FAHR., or in boiling water (83.), but much more slowly. It also appears that the substance *in a finely divided state* loses its heating power with much greater rapidity than when in a *massive form*; in the former case it requires only a few months, while in the latter case it requires at least several years (26.); but whether this difference is due to the difference of cohesion or to the difference of amount of exposed surface of the substance, I have not ascertained.

k. *Miscellaneous observations.*

88. A small quantity of mercury in a gutta-percha capsule, was made the cathode in the tartaric acid solution (2.), and a deposit of grey antimony formed upon it; a peculiar appearance and disappearance of metallic films upon the surface of the mercury occurred on discontinuing and renewing the electric current, apparently caused by deposition of films of antimony and absorption of the films by the mercury; this was repeated many times until accumulation of antimony in the mercury interfered. By passing a continuous feeble electric current into the mercury, a compound of that metal and antimony, of a pasty consistence, was formed, which gradually spread (in an arborescent form interspersed by warty excrescences) by capillary action all over the inner and outer surfaces of the small capsule, and transferred the remaining fluid mercury over the edge of the capsule into the depositing vessel. If ordinary chloride of antimony was substituted for the tartaric acid liquid, the whole of the deposited black bright antimony remained unabsorbed upon the surface of the mercury, and exhibited the cohesive action (17.) strongly, as long as the deposit was sufficiently thin.

89. In addition to the liquid already mentioned (2.) for obtaining grey crystalline antimony, the grey metal may be readily obtained by partly saturating hydrofluoric acid with tartar-emetic or oxide of antimony, and acting upon the liquid in the usual manner. Also by placing fragments of antimony with  $2\frac{1}{2}$  parts of hydrofluoric acid in a gutta-percha cup, and adding to them in small portions at a time about one part of nitric acid; and when the metal has ceased to dissolve, electrolysing the solution by a battery of moderate power. Each of these liquids yields crystalline antimony freely, but in neither instance has the metal the peculiar heating property.

90. The best liquid I have yet found for forming bars, &c. of the active variety, is composed of one avoirdupois ounce of teroxide of antimony (or of oxychloride of antimony) dissolved in five or six ounces by measure of pure hydrochloric acid of sp. gr. 1.12. Bars are formed by depositing the substance upon narrow strips of sheet silver, the edges of which are enclosed by vertical borders of white wax. To remove safely the bars from the moulds within which they are deposited, the latter are placed (after being well washed with water and the aid of a soft brush) upon a surface of gutta percha in ice-cold water, and the walls of wax carefully removed in portions at a time. Inconvenient projections of the metal are removed by means of a small pair of nippers in *minute* portions at a time, with the greatest caution, in the cold water. *Cutting* action with this tool is apt to discharge the heat of the metal, whilst *slow lever* action will frequently remove projections one-twelfth of an inch thick with safety.

### 1. *Recapitulation.*

91. From the experiments and observations recorded in this paper, it appears—that the heat evolved by electro-deposited antimony is not due to cohesive action (63.), nor to alteration of the specific heat of the substance (66.):—the temperature at which the sudden discharge occurs varies from  $170^{\circ}$  to upwards of  $212^{\circ}$  FAHR. (69. 70.):—the total amount of heat evolved by electro-deposited antimony is usually sufficient to raise the temperature of an equal weight of ordinary antimony about 650 FAHR. degrees (73.):—the evolution of vapour of terchloride of antimony is not a *cause* but an *effect* of the heat (75):—the amount of heat evolved is greater at high temperatures than at low ones (77.), similar to the *specific* heat of substances:—the active substance consists of about 93.5 per cent. of antimony, 6.0 per cent. of terchloride of antimony, 0.3 per cent. of hydrochloric acid, and a trace of water (81.); it is also liable to contain traces of nearly all the impurities of the anode and of the depositing liquid (78.):—the discharge of heat is always attended by a diminution of attraction between the metal and its associated terchloride of antimony (84.):—the terchloride of antimony cannot apparently be extracted without destroying the heating property of the substance (85.):—and by lapse of time the active substance invariably loses its heating power, especially if it is in a state of minute division (87.).